

SCIENCE FOR GLASS PRODUCTION

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ZINC OXIDE IN BORATE GLASS-FORMING SYSTEMS

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Glasses based on the system $\text{ZnO} - \text{SrO} - \text{B}_2\text{O}_3$ with additional introduction of PbO , Al_2O_3 , and Li_2O are investigated; an elemental analysis of the heterogeneities is performed. The effect of ZnO on the physicochemical properties of glasses is considered. Fluxes with a decreased PbO content are developed.

The environmental problems of the synthesis of low-melting glasses (fluxes) for decorating glass articles with an application temperature of $580 \pm 10^\circ\text{C}$ are caused by their high content of toxic lead oxide (50 – 80 wt.%) [1]. Therefore, the problem of protection from the toxic effect of PbO arise at the stages of batch preparation, glass melting, as well as in the production of finely dispersed powder for preparing pigments. Consequently, developing new low-melting glass compositions with a decreased content of lead oxide is topical.

The most promising in this respect are glasses based on zinc-bearing borate systems with a low content of SiO_2 : not more than 10% (here and elsewhere molar content, unless otherwise specified).

In the opinion of B. V. Nekrasov [2], the toxicity of zinc compounds is relatively low. According to some data, zinc compounds by themselves are not toxic, whereas their toxic effect is caused by impurities contained in them.

As we have earlier demonstrated [3], in the binary system $\text{ZnO} - \text{B}_2\text{O}_3$ one can expect that the effect of zinc oxide on the properties of borate glasses is the highest compared to other oxides of bivalent metals. Thus, ZnO due to its ionic potential value should exceed PbO and all oxides of alkaline-earth materials in its effect on the coefficient of linear thermal expansion (TCLE) in the range of inflections on the composition – property curves of binary borate glasses (Fig. 1).

It is notable that glasses in the zinc-borate system are formed with a substantial content of ZnO — up to 62% [4]. Their melting temperature is no higher than 1100°C .

According to the data in [4], glass-forming properties in the $\text{ZnO} - \text{B}_2\text{O}_3$ system are the most obvious when the ZnO content is 45 – 60% and, accordingly, the B_2O_3 content is

40 – 55%, i.e., with their approximately equal quantities. Melts with a lower content of ZnO are prone to clearly manifested liquation involving separation into two layers and after cooling form a heterogeneous two-layer glass. At the same time, the lowest-melting eutectic in this system, which facilitates the stability of the vitreous state, corresponds to a ZnO content of approximately 60%. Therefore, it was logical to preserve the specified ratio in more complex systems as well ($\text{ZnO} : \text{B}_2\text{O}_3$ from 1.0 : 1.0 to 1.5 : 1.0).

However, the respective glass compositions in the binary system have very low TCLE values; consequently, the resulting fluxes cannot be used in silicate paints.

TCLE of zinc-borate glasses [4]

Content of ZnO , %	TCLE, 10^{-7} K^{-1}
50.0	49.0
55.0	49.0
55.2	52.8
56.0	52.1
59.8	51.9
60.0	48.0
56.2	46.4
59.9	41.1

To increase the TCLE, it was necessary to introduce an oxide with a larger cation into the glass composition. The oxide selected in this capacity was SrO .

Thus, the synthesis of low-melting low-lead fluxes is based on the system $\text{ZnO} - \text{SrO} - \text{B}_2\text{O}_3$ complicated by invariable (20%) additives of PbO , Al_2O_3 , and Li_2O . The content of ZnO and B_2O_3 varied from 25 to 45% and SrO content from 10 to 30%.

The behavior of ZnO in borate systems generates special interest, since it can make part of a glass composition in an

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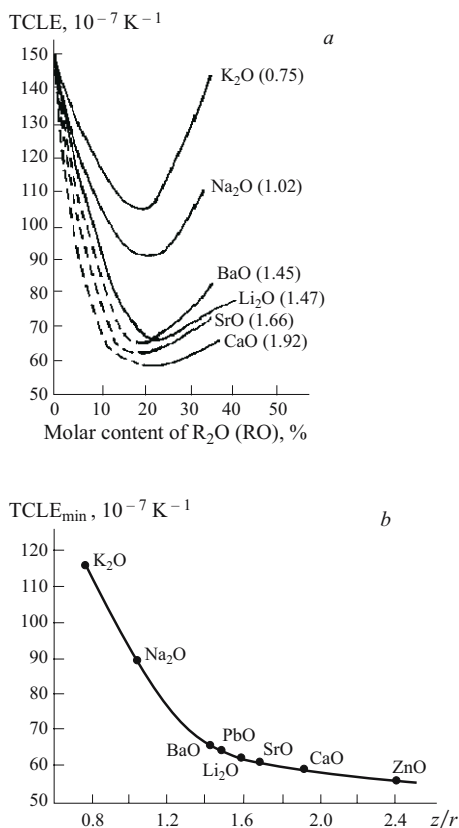


Fig. 1. Dependence of TCLE of borate glasses on R_2O (RO) content (a) and minimal TCLE values of binary borate glasses depending on ionic potential of cation z/r (b).

equal or larger quantity than the main glass-forming agent, i.e., B_2O_3 .

All glasses in the investigated system melt and clarify well at the temperatures of $1000 - 1100^\circ\text{C}$. However, glasses with ZnO content of 35% or more and a low content of SrO resulted opacified. Analysis of these glasses using a JSM-5610LV scanning electron microscope with system of chemical analysis EDXJED-2201 JEOL (Japan) identified the presence of heterogeneities (about 5%) of size $10 - 50 \mu\text{m}$ ($\times 200$). At higher magnification it was discovered that these heterogeneities are clusters of crystals of size $0.2 \mu\text{m}$ (Fig. 2).

The elemental analysis of these clusters identified the presence of the following elements (atomic content, %; with wt.% indicated in brackets): O 40.18 (53.01), Al 21.02 (11.30), Zn 24.16 (24.61), Sr 3.73 (2.62), and Pb 10.91 (8.45). By their chemical composition the registered heterogeneities can be attributed to crystals of the gahnite type $\text{ZnO} \cdot \text{Al}_2\text{O}_3$ and the small impurities of SrO and PbO presumably correspond to the vitreous interlayers between the crystals.

The elemental analysis of glass revealed a decreased content of aluminum and zinc atoms compared to their content based on synthesis (atomic weight, %; wt.% in brackets): O 34.30 (41.75), Al 4.12 (2.18), Zn 23.17 (24.75),

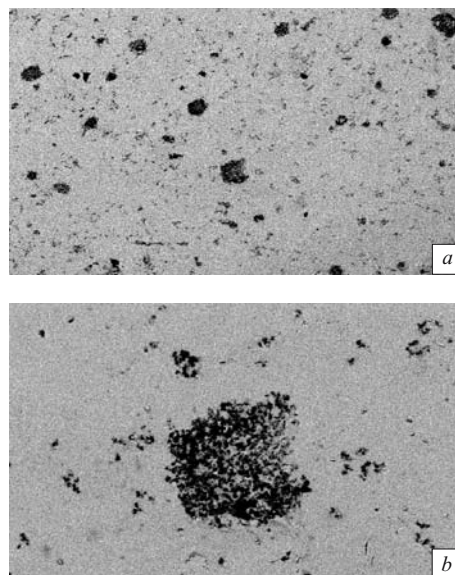


Fig. 2. Electron microscope studies of opacified glass at magnifications $\times 100$ (a) and $\times 500$ (b).

Sr) 10.55 (8.76), and Pb 27.94 (22.56). No liquation phenomena were observed in glass.

Under heat treatment of glasses in a gradient furnace within a temperature interval of $500 - 900^\circ\text{C}$, it was established that all crystals are resistant to crystallization including opacified glasses. Glass-spreading temperatures determined by the position of the so-called zero meniscus on a ceramic boat are within the limits of $550 - 900^\circ\text{C}$.

The dependence of glass properties on their composition in the system was considered earlier [5]. The present paper analyzes the effect of replacing B_2O_3 by ZnO on glass structure and properties with 10 and 15% SrO content and a constant content of other components.

The softening temperature and microhardness of glasses depends on the overall strength of chemical links in glass. It can be seen from Fig. 3 that with increasing content of ZnO instead of B_2O_3 , the softening temperature and microhardness decrease, which can be caused by a decreased degree of cohesion of the structural glass lattice due to the decreased content of the glass-forming agent and possible structural transformations upon introducing ZnO. It should be noted that the curves for glasses containing 15% SrO are positioned above the curves for glasses with 10% content, i.e., SrO in this case has a reverse effect and leads to a certain increase in the overall strength of links in borate glass. The strontium ion as a large cation (its ionic radius is 0.12 nm) should facilitate the transformation of part of the $[\text{BO}_3]$ groups into $[\text{BO}_4]$ groups, which produces a certain increase in the degree of structural cohesion.

The effect of ZnO on the structure of glasses in this system is not so unambiguous. First, the results of electron microscope analysis of experimental glasses show that part of ZnO actively binds with Al_2O_3 forming gahnite and replac-

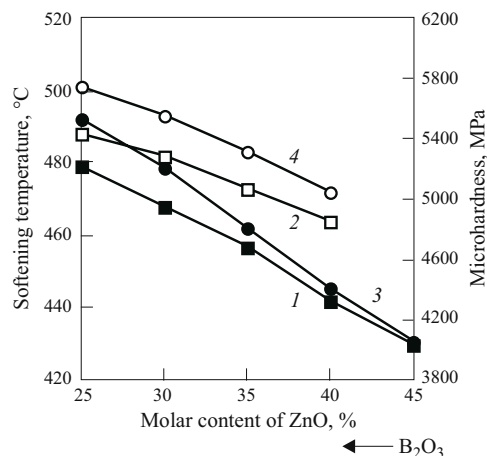


Fig. 3. Dependence of softening temperature and microhardness of glasses on ZnO content: 1 and 2) softening temperature for SrO content equal to 10 and 15%, respectively; 3 and 4) microhardness for 10 and 15% SrO, respectively.

ing the aluminoborate component in the glass structure. Second, the deterioration of glass properties, as the ZnO content grows at the expense of B_2O_3 , indicates the overall decrease in the total strength of links in the glass.

Figure 4 shows the IR spectra of experimental glasses. They exhibit absorption bands in the ranges of: $1360 - 1300 \text{ cm}^{-1}$ (the first band, whose intensity virtually does not change), $1250 - 1190 \text{ cm}^{-1}$ (the second band, emerging with over 30% ZnO; its intensity grows as ZnO content increases to 45%), $1040 - 1000 \text{ cm}^{-1}$ (the third band persisting up to 40% content of ZnO), $955 - 928 \text{ cm}^{-1}$ (the fourth band, emerging with 35% ZnO and becoming more intense up to its content of 45%); and $700 - 715 \text{ cm}^{-1}$ (deformation band of borate glasses that is little dependent on glass structure — the fifth band).

Absorption bands 1 – 4 gradually shift toward lower frequencies, as the content of ZnO increases.

The first two bands correspond to three-coordination boron. The absorption band at $1300 - 1360 \text{ cm}^{-1}$ is determined by the presence of $[BO_3]$ groups with bridge links between them, whereas the band at $1119 - 1250 \text{ cm}^{-1}$ is presumably related to the emergence of chains of the type $B(III) - O - B(IV)$ with nonbridge links. The calculation of the coordination number of boron based on the absorption band of $1300 - 1360 \text{ cm}^{-1}$ using the Dehill and Roy formula confirms that this band is related precisely to three-coordination boron (estimated coordination number is 3.01 – 3.30). A decrease in B_2O_3 content to 25% and an increase in ZnO content to 45% surely cannot ensure 3D or planar coupling of $[BO_3]$ groups. The coordination number of boron grows to some extent with introduction of a large quantity of ZnO, but mainly due to the incorporation of six-coordination zinc into the structure complexes.

The third and the fourth absorption bands are interpreted as corresponding to groups $[BO_4]$. However, the estimated

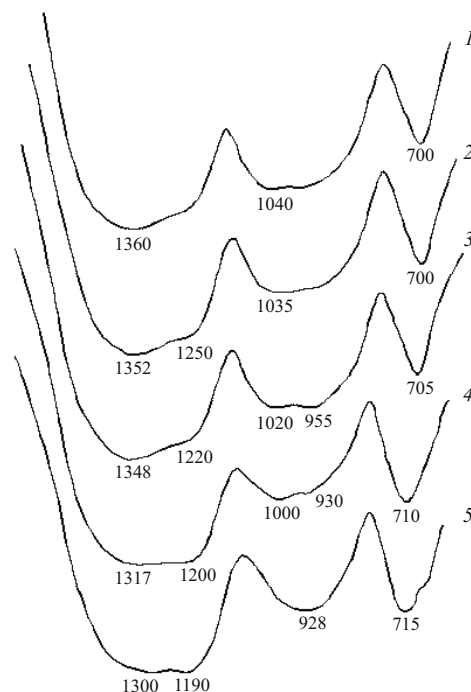


Fig. 4. IR spectra of glasses with molar content of ZnO and B_2O_3 , respectively, equal to 25 and 45% (1), 30 and 40% (2), 35 and 35% (3), 40 and 30% (4), 45 and 25% (5).

coordination number in this case is somewhat higher than 4, namely 5.1 – 5.4. This may be due to the active formation of zinc-borate complexes with absorption bands shifting from 1040 to 1000 and from 955 to 928 cm^{-1} , as well as the formation of end groups $>B - O^-$ (the band at $1190 - 1250 \text{ cm}^{-1}$). Absorption bands in the same range ($900 - 1100 \text{ cm}^{-1}$) were identified in zinc metaborate $4ZnO \cdot 3B_2O_3$ [6].

Consequently, a complex structure with the combination of groups $[BO_3]$, $[BO_4]$ with bridge and nonbridge oxygen ions, end groups $>B - O^-$, and zinc-borate complexes is formed in experimental glasses. Zinc oxide has a weak effect on the coordination transformation $[BO_3] \rightarrow [BO_4]$, but is capable of forming its own structure of zinc-borate complexes.

Thermal expansion of experimental glasses varies significantly with increasing content of ZnO; it is equal to $(73 - 75) \times 10^{-7} \text{ K}^{-1}$ with 10% SrO and to $(78 - 81) \times 10^{-7} \text{ K}^{-1}$ with 15% SrO. This is also confirmed by the fact that ZnO has no significant effect on the structural state of borate groups, since partial TCLE values for three- and four-coordination boron are different.

Based on the set of properties, experimental glasses that are the most suitable as fluxes for silicate paints have the following characteristics: softening temperature 435°C , spreading temperature 550°C , TCLE $76.5 \times 10^{-7} \text{ K}^{-1}$, density 3671 kg/m^3 , and microhardness 2774 MPa .

The compositions proposed for low-melting low-lead fluxes have been tested in industrial conditions at the Borisovskii Crystal Works and are recommended as fluxes for silicate paints.

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